



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08L 67/02, 77/00, A63B 37/00	A1	(11) International Publication Number: WO 92/12206 (43) International Publication Date: 23 July 1992 (23.07.92)
(21) International Application Number: PCT/US91/09168 (22) International Filing Date: 17 December 1991 (17.12.91) (30) Priority data: 634,793 27 December 1990 (27.12.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: BRAEMER, Jon, Paul ; 1019 Wagoner Drive, Wilmington, DE 19805 (US). HAGMAN, John, Francis ; 1903 Brant Road, Wilmington, DE 19810 (US). STATZ, Robert, Joseph ; 115 Beverly Drive, Kennett Square, PA 19348 (US).		(74) Agents: EVANS, Craig, H. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>
(54) Title: COMPOSITIONS USEFUL IN THE MANUFACTURE OF GOLF BALLS (57) Abstract The invention provides compositions useful in the manufacture of one-, two- and three-piece golf balls comprising blends of a copolyetherester or copolyetheramide, an epoxy-containing compound, and an acid-containing ethylene copolymer ionomer.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	RU	Russian Federation
CG	Congo	KP	Democratic People's Republic of Korea	SD	Sudan
CH	Switzerland	KR	Republic of Korea	SE	Sweden
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
DE	Germany	MC	Monaco	TG	Togo
DK	Denmark			US	United States of America

TITLE OF THE INVENTION

COMPOSITIONS USEFUL IN THE MANUFACTURE OF GOLFBALLS

FIELD OF THE INVENTION

5 The subject invention relates to the manufacture of one-, two-, and three-piece golfballs, particularly with respect to polymer blend compositions useful therein.

10

BACKGROUND OF THE INVENTION

 There currently exist two general types of premium golfballs: a "three-piece" ball which comprises a spherical molded center, having an elastomeric thread-like material wound around it, covered with
15 either a thermoplastic or thermoset material; and a "two-piece" ball which comprises a spherical molded core covered with a thermoplastic material. The material used to mold the three-piece centers and the two-piece
20 cores has traditionally been a thermoset rubber, for example, polybutadiene rubber. As with any thermoset material, however, there are major disadvantages, such as the inability to recycle scrap materials and the need for complex multistep manufacturing processes. Of
25 course, three-piece balls and two-piece balls are by their very nature more complicated and costly to manufacture than the long sought after one-piece golfball, which has yet to be successfully demonstrated except for limited flight golfballs.

 In an effort to overcome the deficiencies of
30 the traditional thermoset three-piece centers and two-piece cores, and in the quest to produce a one-piece golfball, attempts have been made to utilize certain thermoplastic materials in the molding of such centers, cores and one-piece balls, but with limited success.
35 For example, U.K. Patent Application 2,164,342A

describes moldable compositions comprising ionic
c polymers (or potentially ionizable acid copolymers)
blended with certain thermoplastic materials such as a
polyester block copolyamide, a polyether copolyamide, a
5 copolyester and the like. Those compositions are said
to be useful as three-piece centers, two-piece cores and
one-piece solid golfballs, but they lack, e.g.,
durability. Therefore, there still exists the need for
a material that is thermoplastic, yet resilient and
10 durable enough, and imparting adequate compression, to
be useful as a three-piece center, two-piece core and a
one-piece golfball.

SUMMARY OF THE INVENTION

The subject invention provides thermoplastic
15 compositions that can be used in the manufacture of
one-, two- and three-piece golfballs. More
specifically, the subject invention comprises a
composition for the manufacture of a one-piece golfball
comprising 40-65 polymer weight percent of a
20 thermoplastic polymer selected from copolyetheresters
and copolyetheramides; 1-10 polymer weight percent of an
epoxy-containing compound; 5-20 total weight percent of
a filler having a density greater than or equal to about
4 gm/cc, and the remainder, to total 100 polymer weight
25 percent, of an acid-containing ethylene copolymer
ionomer.

In another embodiment, the subject invention
provides a two-piece golfball in which the core
comprises 50-65 weight percent of a thermoplastic
30 polymer selected from copolyetheramides and
copolyetheresters; 1-10 weight percent of an
epoxy-containing compound; and the remainder, to total
100 percent, of an acid-containing ethylene copolymer
ionomer; preferably provided that the thermoplastic
35

polymer is present in greater than 50 volume percent of the composition.

In another embodiment, the subject invention provides a two-piece golfball in which the core comprises between 30 and 50 polymer weight percent of a thermoplastic polymer selected from copolyetheramides and copolyetheresters; 1-10 polymer weight percent of an epoxy-containing compound; 15-25 total weight percent of a filler having a density greater than about 5 gm/cc; and the remainder, to total 100 polymer weight percent, of an acid-containing ethylene copolymer ionomer.

In yet another embodiment, the subject invention provides a three-piece golfball in which the center comprises 65-90 weight percent of a thermoplastic polymer selected from copolyetheramides and copolyetheresters; 1-10 weight percent of an epoxy-containing compound; and the remainder, to total 100 weight percent of an acid-containing ethylene copolymer ionomer.

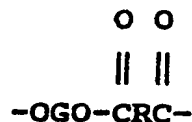
DETAILED DESCRIPTION OF THE INVENTION

Because the species and relative ratios of the components used in the practice of the subject invention vary somewhat depending upon the type of golfball desired (i.e., one-piece, two-piece or three-piece), it is useful to first consider the components themselves.

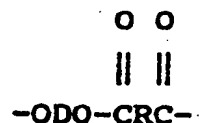
COMPONENT DESCRIPTION

The thermoplastic polymer component of the subject invention is selected from copolyetheresters and copolyetheramides, both classes of polymers being well known in the art. The copolyetheresters are discussed in detail in, e.g., U.S. Patents 3,651,014; 3,766,146; and 3,763,109. They are comprised of a multiplicity of recurring long chain units and short chain units joined head-to-tail through ester linkages, the long chain units being represented by the formula

- 4 -

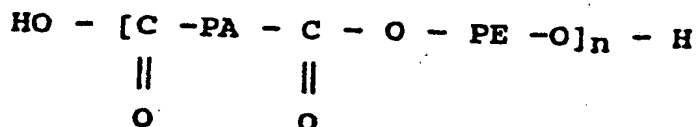


5 and the short chain units being represented by the formula



10 where G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide) glycol having a molecular weight of about 400-6000 and a carbon to oxygen ratio of about 2.0-4.3; R is a divalent radical remaining after removal of hydroxyl groups from a dicarboxylic acid having a
15 molecular weight less than about 300; and D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight less than about 250; provided said short chain ester units amount to about 15-95 percent by weight of said
20 copolyetherester. The preferred copolyetherester polymers are those where the polyether segment is obtained by polymerization of tetrahydrofuran and the polyester segment is obtained by polymerization of tetramethylene glycol and phthalic acid. Of course, the
25 more polyether units incorporated into the copolyetherester, the softer the polymer. For purposes of the subject invention, the molar ether:ester ratio can vary from 90:10 to 10:90, preferably 80:20 to 60:40; and the shore D hardness is less than 70, preferably
30 about 40. The copolyetheramides are also well known in the art as described in, e.g., U.S. 4,331,786. They are comprised of a linear and regular chain of rigid polyamide segments and flexible polyether segments, as represented by the general formula

35



5 wherein PA is a linear saturated aliphatic polyamide
 sequence formed from a lactam or aminoacid having a
 hydrocarbon chain containing 4 to 14 carbon atoms or
 from an aliphatic C₆-C₉ diamine, in the presence of a
 chain-limiting aliphatic carboxylic diacid having 4-20
 carbon atoms; said polyamide having an average molecular
 10 weight between 300 and 15,000; and PE is a
 polyoxyalkylene sequence formed from linear or branched
 aliphatic polyoxyalkylene glycols, mixtures thereof or
 copolyethers derived therefrom said polyoxyalkylene
 glycols having a molecular weight of less than or equal
 15 to 6000 and n indicates a sufficient number of repeating
 units so that said polyetheramide copolymer has an
 intrinsic viscosity of from about 0.8 to about 2.05.
 The preparation of these polyetheramides comprises the
 step of reacting a dicarboxylic polyamide, the COOH
 20 groups of which are located at the chain ends, with a
 polyoxyalkylene glycol hydroxylated at the chain ends,
 in the presence of a catalyst such as a
 tetraalkylorthotitanate having the general formula
 Ti(OR)₄, wherein R is a linear branched aliphatic
 25 hydrocarbon radical having 1 to 24 carbon atoms. Again,
 the more polyether units incorporated into the
 copolyetheramide, the softer the polymer. The
 ether:amide ratios are as described above for the
 ether:ester ratios, as is the shore D hardness.

30 The epoxy-containing compound component of the
 subject invention can be any compound that has an epoxy
 functionality readily available for reaction with the
 carboxylic acid groups in the ethylene copolymer
 ionomers detailed below. Such compounds include, for
 35 example, epoxidized oils such as epoxidized soy bean

oil, epoxidized elastomers such as epoxidized natural rubber or epoxidized polybutadiene rubber, or an epoxy-containing copolymer E/X/Y wherein E is ethylene, X is a softening comonomer, for example, an acrylate, methacrylate, vinyl ether or vinyl ester comonomer present in 0-50 (preferably 0-35, most preferably 0-30) weight percent of the polymer, and Z is an epoxy-containing vinyl unsaturated monomer present in 1-25 (preferably 1-20, most preferably 1-15) weight percent of the polymer; such copolymers include without limitation, ethylene copolymers copolymerized with one or more reactive monomers selected from unsaturated epoxides of 4-11 carbon atoms, such as glycidyl acrylate, glycidyl methacrylate, and vinyl glycidyl ether, and optionally additionally containing alkyl acrylate, alkyl methacrylate, carbon monoxide, sulfur dioxide and/or alkyl vinyl ether, where the alkyl radical is from 1-12 carbon atoms. Preferred glycidyl containing copolymers for use in the compositions of the present invention include ethylene/glycidyl acrylate, ethylene/n-butyl acrylate/glycidyl acrylate, ethylene/methyl acrylate/glycidyl acrylate, ethylene/glycidyl methacrylate, ethylene/n-butyl acrylate/glycidyl methacrylate and ethylene/methyl acrylate/glycidyl methacrylate copolymers. The most preferred glycidyl-containing copolymers are ethylene/n-butyl acrylate/ glycidyl methacrylate and ethylene/glycidyl methacrylate copolymers.

These glycidyl-containing ethylene copolymers are made by processes well known in the art, e.g., by direct copolymerization of ethylene, glycidyl methacrylate or glycidyl acrylate, and the above-defined acrylate or methacrylate in the presence of a free-radical polymerization initiator at elevated temperatures, preferably 100°-270°C. and most preferably

130°-230°C, and at elevated pressures, preferably at least 70 MPa, and most preferably 140-350 MPa.

The acid-containing ethylene copolymer ionomer component of the subject invention includes E/X/Y copolymers where E is ethylene, X is a softening comonomer such as acrylate or methacrylate present in 0-50 (preferably 0-25, most preferably 0-2) weight percent of the polymer, and Y is acrylic or methacrylic acid present in 5-35 (preferably 10-35, most preferably 15-35) weight percent of the polymer, wherein the acid moiety is neutralized 1-90% (preferably at least 40%, most preferably at least about 60%) to form an ionomer by a cation such as lithium*, sodium*, potassium, magnesium*, calcium, barium, lead, tin, zinc* or aluminum (*= preferred), or a combination of such cations. Specific acid-containing ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/methacrylic acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, and ethylene/acrylic acid/n-butyl methacrylate. Preferred acid-containing ethylene copolymers include ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/methacrylic acid/n-butyl acrylate, ethylene/acrylic acid/n-butyl acrylate, ethylene/methacrylic acid/methyl acrylate and ethylene/acrylic acid/methyl acrylate copolymers. The most preferred acid-containing ethylene copolymers are ethylene/methacrylic acid, ethylene/acrylic acid, ethylene/(meth)acrylic

acid/n-butyl acrylate, ethylene/(m th)acrylic acid/ thyl
acrylat , and ethylene/(m th)acrylic acid/methyl
acrylate copolymers. The manner in which the ionomers
are made is well known in the art as described in, e.g.,
5 U.S. 3,262,272 (Rees).

The optional filler component of the subject
invention is chosen to impart additional density to
blends of the previously described components, the
selection being dependent upon the type of golfball
10 desired (i.e., one-piece, two-piece or three-piece), as
will be more fully detailed below. Generally, the
filler will be inorganic having a density greater than
about 4 gm/cc, preferably greater than 5 gm/cc, and will
be present in amounts between 5 and 65 weight percent
15 based on the total weight of the polymer components.
Examples of useful fillers include zinc oxide, barium
sulfate, lead silicate and tungsten carbide, as well as
the other well known corresponding salts and oxides
thereof. It is preferred that the filler materials be
20 non-reactive with the polymer components described
above. Additional optional additives useful in the
practice of the subject invention include acid copolymer
waxes (e.g., Allied wax AC143 believed to be an
ethylene/16-18% acrylic acid copolymer with a number
25 average molecular weight of 2,040) which assist in
preventing reaction between the filler materials (e.g.,
ZnO) and the acid moiety in the ethylene copolymer; TiO₂
which is used as a whitening agent; optical brighteners;
surfactants; processing aids; etc.

30 The specific combinations of components used
in the practice of the subject invention will in large
part be dependent upon the type of golfball desired
(i.e., one-piece, two-piece or three-piece), as detailed
below.

35

**THREE-PIECE GOLFBALL
PREFERRED EMBODIMENTS**

As used herein, the term "three-piece ball" refers to a golfball comprising a center made from the compositions of the invention, a traditional elastomeric winding wound around the center, and a cover made from any traditional golfball cover material such as Surlyn ionomer resin, balata rubber and the like. These three-piece golfballs are manufactured by well known techniques as described in, e.g., U.S. 4,846,910.

For purposes of the subject invention, the center is made by injection molding of the compositions of this invention. Those centers are then placed into a winding machine in which the end of an elastomeric thread is affixed to the molded center and the thread wound around the center to a predetermined thickness. A dimple-patterned cover is then molded around this wound center. For use as the center material for three-piece balls, the preferred composition of the subject invention comprises 65-90 weight percent of the thermoplastic component, 1-10 weight percent of the epoxy-containing compound and the remainder, to total 100 weight %, of the acid-containing ethylene copolymer ionomer. The most preferred compositions of the invention for use as a three-piece center also contain about 40-60 weight percent of the previously described filler material, based on total weight of the three polymer components plus filler. The most preferred thermoplastic component for use in the three-piece ball is a copolyetherester; the most preferred epoxy-containing compound is a glycidyl-containing ethylene copolymer; and the most preferred acid-containing ethylene copolymer ionomer is an ethylene/methacrylic acid or ethylene/acrylic acid copolymer. The three-piece ball that performs most

satisfactorily, as seen in the Examples below, contains a center molded from a composition that comprises from about 35 weight percent (total composition) of the polyetherester, described in Table 1 below as "H1", 1-5 weight percent of an ethylene/n-butylacrylate (28%)/glycidyl methacrylate (8%) copolymer, about 10 weight percent of an ethylene/methacrylic acid (20%) copolymer highly neutralized with Na cations to form the ionomer, about 50 weight percent ZnO, and about 5 weight percent Allied wax AC143. Note that these weight percentages are given as a percent based on total composition to more clearly show the relative proportion of components in an actual three-piece center formulation.

TWO-PIECE GOLFBALL PREFERRED EMBODIMENTS

As used herein, the term "two-piece ball" refers to a golfball comprising a core made from the compositions of the invention, and a cover made from any traditional golfball cover material as discussed above. These two-piece balls are manufactured by first molding the core from the compositions of the subject invention, positioning these preformed cores in an injection molding cavity using retractable pins, then injection molding the cover material around the core. The most efficient way to produce two-piece golf balls is to use runnerless molding techniques, preferably valve gated, where the polymer is injection molded into the cavity at the pole or poles instead of the equator as is commonly done. The valve gate is disguised as a dimple in the ball. This technology greatly improves the efficiency and cost of producing two-piece golf balls as the runners are eliminated, as is all of the effort and cost relative to rework. For use as the core material for

two-piece balls, on preferred composition of the subject invention comprises 50 to 65 polymer weight percent of the thermoplastic component, 1-10 polymer weight percent of the epoxy-containing compound, and the remainder to total 100 weight percent, of the acid-containing ethylene copolymer ionomer; preferably provided that the thermoplastic component is present in greater than 50 volume percent of the composition. It is also preferred that such compositions contain 15-25 total weight percent of the previously described filler material. In another preferred composition, the thermoplastic component is present between 30 and 50 polymer weight percent, the epoxy-containing component present between 1 and 10 polymer weight percent, and the ionomer the remainder to total 100 weight percent, but in such a composition the filler material is necessarily present in 15-25 weight percent based on total composition, and must have a density of greater than about 5 gm/cc (e.g., zinc oxide, lead silicate or tungsten carbide). In both embodiments, the most preferred thermoplastic component is a copolyetherester; the most preferred epoxy-containing compound is a glycidyl-containing ethylene copolymer; and the most preferred acid-containing ethylene copolymer ionomer is an ethylene/(meth)acrylic acid copolymer. The two-piece ball that performs most satisfactorily, as seen in the Examples below, contains a core molded from a composition that comprises 50-60 polymer weight percent of the polyetherester described in Table 1, 1-5 polymer weight percent of an ethylene/n-butyl acrylate (28%)/glycidyl methacrylate (5%) copolymer, 40-45 polymer weight percent of an ethylene/(meth)acrylic acid (20%) copolymer highly neutralized with Na cations to form the ionomer, about 20 total weight percent ZnO, and about 5 weight percent Allied wax.

**ONE-PIECE GOLFBALL
PREFERRED EMBODIMENTS**

As used herein, the term "one-piece ball" refers to a golfball molded in toto from the compositions of the subject invention, i.e., not having elastomeric windings nor a cover. The one-piece molded ball will have a traditional dimple pattern and may be coated with a urethane lacquer or be painted for appearance purposes. These one-piece balls are manufactured by direct injection molding techniques under conditions described below in Table 2B. For use in one-piece balls, the preferred composition of the subject invention comprises 40 to 65 polymer weight percent of the thermoplastic component, 1-10 polymer weight percent of the epoxy-containing compound, 5-20 weight percent, based on the total weight percent, of the previously described filler material and the remainder, to total 100 polymer weight percent, of the acid-containing ethylene copolymer ionomer. Again, the most preferred thermoplastic component is a copolyetherester; the most preferred epoxy-containing compound is a glycidyl-containing ethylene copolymer; and the most preferred acid-containing ethylene copolymer ionomer is an ethylene/methacrylic acid copolymer. The one-piece ball that performs the most satisfactorily, as seen in the Examples below, is molded from a composition of the subject invention comprising about 55 polymer weight percent of the polyetherester described in Table 1, 1-5 polymer weight percent of ethylene/n-butyl acrylate (28%)/glycidyl methacrylate (8%) copolymer, 40-45 polymer weight percent of an ethylene/methacrylic acid (20%) copolymer highly neutralized with Na cations to form the ionomer, about 10 total weight percent ZnO, about 5 total weight

percent AC143 Allied wax, and about 5 total weight percent TiO_2 .

Those skilled in the art will appreciate that certain variations of the compositions of the subject invention will also be useful in the manufacture of one-piece and two-piece restricted flight golfballs, also commonly known as range balls; the distance that such range balls can travel being dependent upon the resiliency of the materials used and the compression imparted. Further, the compositions of the subject invention having flex modulus of about 14,000-30,000 (ASTM D790, procedure B), preferably without filler, may also be employed as golfball cover materials.

TESTING CRITERIA

In the Examples set out below, a number of testing criteria are utilized in the evaluation of golfball performance: percent rebound, total distance travelled, initial velocity, coefficient of restitution (COR) and compression. Percent rebound is determined by dropping the ball (or three-piece center/two-piece core) from a height of 100 inches and measuring the rebound from a hard, rigid surface such as a thick steel plate or a stone block; an acceptable result is about 65-80%. Total distance is determined by striking a ball with a 10.5 degree loft driver at a clubhead speed of 95 mph; an acceptable result is about 220-250 yds. Initial velocity is the measured speed of the ball off a clubhead as described for total distance (acceptable result approaching but less than 215 ft/sec as used in Table 2A) or the measured speed of the ball when hit at 230 feet per second by an implement having a face angle of 13° with respect to the vertical (acceptable result approaching but less than 255 ft/sec as used in Table 1C). COR is measured by firing a golfball (or two piece core) from an air cannon at a velocity determined

by the air pressure. The initial velocity generally employed is between 125 to 255 feet/sec. The ball strikes a steel plate positioned three feet away from the point where initial velocity is determined, and rebounds through a speed-monitoring device. The return velocity divided by the initial velocity is the COR; acceptable results are .550-.750 at 180 ft/sec or .500-.650 at 230 ft/sec. Compression is defined as the resistance to deformation of a golfball, measured using an ATTI machine; an acceptable result is about 70-120.

EXAMPLES 1, 2, 3; COMPARATIVE EXAMPLES C1, AND C2; AND CONTROL EXAMPLE.

These examples and comparative examples illustrate the preparation and properties of centers for three-piece golf balls and of finished balls from such centers. Blends for the thermoplastic centers of such balls were prepared by extrusion in a twin screw extruder. The compositions are given in Table 1, and extrusion conditions shown in Table 1A. These blends were then molded into spheres of 1.08 in. diameter using an 8 oz. Van Dorn Injection molding machine, with molding conditions shown in Table 1B. Density and percent rebound were measured on these centers. The centers were also made into three piece balls using conditions similar to those described in U.S. Pat. No. 4,846,910 to Acushnet Corp., by winding with natural rubber threads, and compression molding a cover on top of the windings using a Surlyn® ionomer blend. As a control, the properties of an Acushnet 'Titleist DT' ball are shown. This ball is made of a crosslinked (non thermoplastic) polybutadiene center, natural rubber windings and the same ionomer cover used for the thermoplastic center balls. All property measurements are shown in Table 1C.

TABLE I: CENTER COMPOSITIONS

Ex#	Ref#	Hytrel(H1)	EBAGMA(G1)	Ionomer	Filler	Additive
1	62-4	35(78)	3(4)	I1,8(18)	F1,51	A1
2	62-1	36(75)	2(4)	I1,10(21)	F1,48	A1
5 3	41-5	41(73)	1(2)	I2,14(25)	F1,40	A1
4	10-3	44(73)	1(2)	I2,15(25)	F2,40	-
5	10-2	51(73)	1(2)	I2,18(25)	F2,30	-

10 (Values are weight percentages. Percentages given in parentheses are on a polymer only basis.)

H1 is a 'Hytrel' resin with composition:
18.2/0.3/72.3/9.1:terphthaloyl/TMTM/PTMEG2000/1,4 butane diol, plus an antioxidant. PTMEG is polytetramethyl ne glycol. TMTM is trimethyltrimellitoyl.

15

(G1) Ethylene/28% butyl acrylate/8.4% glycidyl methacrylate with a melt index of 10.6.

20 (I1)Ethylene/20% methacrylic acid, 57% Na neutral., MI=1

(I2)Ethylene/15% methacrylic acid, 52% Li neutral., MI=1.8

25 (F1)Fisher Zinc Oxide

(F2)Wittaker Clark Barium Sulfate, Blanc Fix N

30 (A1)AC143 Ethylene/15.66% acrylic acid with Mn=2040, Mw=5670

TABLE 1A
EXTRUSION CONDITIONS FOR BALL COMPOSITIONS

Screw Speed RPM	Zone 1 Temp°C	Zone 2 Temp°C	Zone 3 Temp°C	Die Temp°C	Rate lbs/hr	Vacuum In
5	150	161	194	202	207	16.4 26
10						
15						
20						
25						
30						
35						

TABLE 1B
MOLDING CONDITIONS FOR THREE PIECE CENTERS*

5	Temperatures Degrees C		
	Rear		174
	Center		177
	Front		177
10	Nozzle		171
	Mold	Fixed	10
		Movable	10
	Pressures Kg/sq.cm.		
15			
	Injection 1st stage		140
	Injection Second Stage		84
	Injection Hold		14
20	Cycle Times Sec:		
	Injection		10
	Hold		300
	Booster		7
25	Screw Retraction		1.75
	Pad (cm)		.05
	Screw Speed (RPM)		55
	Back Pressure (kg/sq.cm)		8.4
30			
	Mold Size 1.092 Inches Diameter (0.429 cm)		
	Part Size 1.08 Inches Diameter (0.425 cm)		
	*Prototype mold, limited cooling, two cavity		
35			

TABLE 1C
PROPERTIES OF THREE PIECE CENTERS OR BALLS

Ex#	-----Center-----			-----Ball-----			
	MI(1)	Density (g/cc)	%Rebound	Compr. ATTI	Wt. (g)	Velocity ft/sec.	%Rej. (2)
1	11.1	1.71	67	85.9	45.2	250.9	0
2	17.6	1.56	69.6	85.9	43.8	251.8	7.1
3	20.0	1.45	67.4	97.2	42.2	252.0	17
C1	17.0	1.48	69.4	94.7	42.6	251.4	68
C2	22.0	1.31	70.5	98.0	41.0	253.0	62
Control			70.0	77.3	45.2	252.8	22.7

(1) Measured using ASTM D1238, with 10 Kg.wt at 220 deg. C.

(2) Percent Reject based on out of roundness as measured by a fluoroscope on finished ball. Out of roundness is caused by the combined effect of pressure due to winding and the heat associated with the compression molding of the cover. Out of round balls behave unsatisfactorily, and would have properties outside USGA standards.

The first three examples show that balls may be made satisfactorily with respect to number of rejects, and these are actually less than in the case of the thermoset center ball control. Compression is somewhat higher than for the control, but within the acceptable range of about 70 to 120. Initial velocity is below the acceptable maximum of 255. The % rebound is comparable to the control center, and an indication of generally acceptable performance. It will be noted however, that the best balls are produced when the EBAGMA level is highest. In the two comparative examples, while measured properties were acceptable, the level of rejects was totally unacceptable. Comparative example C1 has a low level of polyetherester and filler. Comparative example C2 has a very low level of filler.

EXAMPLES 4, 5, AND 6; COMPARATIVE EXAMPLE C3 AND CONTROL EXAMPLE

These examples describe the preparation of blends for the core for two piece golf balls, golf balls made therefrom, and the properties of the cores and finished balls. The composition of these blends is shown in Table 2. The blends were made using extrusion conditions the same as those for three piece center compositions shown in Table 1A. The blends were molded into cores using conditions shown in Table 2B. The core is 1.5 inches in diameter. Balls were prepared by positioning preformed thermoplastic cores in an injection molding cavity. The cores were centrally positioned in the cavity by the use of retractable pins. A cover of mixed 'Surlyn' ionomer resin was then injection molded around the core. Properties of the resultant cores or balls are shown in Table 2A.

TABLE 2
CORE COMPOSITIONS

Ex#	Ref#	Hytrel(H1)	EBAGMA	Ionomer	Filler	Additive
5						
4	72-1	41(53)	G2,3(4)	I1,33(43)	F3,19	A1,4
5	8143-3	42(52)	G2,3(4)	I2,35(44)	F4,20	-
6	115-3	42(55)	G1,1(2)	I1,33(43)	F3,19	A1,4
C3	104-2	21(27)	G3,7(9)	I3,49(64)	F2,22	-
10	C4	016R	43(56)	0	I1,34(44)	F3,19
						A1,4

Values are weight percentages. Percentages given in parenthesis are on a polymer only basis.

15 H 1, G1, I1, I2, A1, F2 as in Table 1.

G2 Ethylene/28% n-butyl acrylate/5.3% glycidyl methacrylate with a melt index of 12.0

G3 Ethylene/34.5% n-butyl acrylate/5.3% glycidyl methacrylate with a melt index of 6.0.

20 I3 Ethylene/15% methacrylic acid, 57% Na neutralized, MI=1.2

F3 Zinc Oxide, grade XX503R, Zinc Corp. of America.

F4 Barium Sulfate, 'Barmite' 4.3 microns, Cyprus Corp.

25

TABLE 2A
PROPERTIES OF TWO PIECE CORES OR BALLS

Ex#	-----Core-----			-----Ball-----			
	Compr. ATTI	Durabil. Hits/Break at/psi	COR	Compr. ATTI	Reb. %	Velocity	COR
							Carry & Roll (yds)
30							
4		17/50,20/40	.638	121	77	209.8	.614
5				118	74	208.0	.582
6				111	74	208.4	.586
C3	122			133	67.8	-	-
C4		4/50,7/40	.635				
CONTROL				111	81	213.5	.641
							249

35

The Control ball is a Ram LP ball which has a thermoset butadiene core and a mixed ionomer cover. Coefficient of restitution for cores was measured at 180 ft/sec. Coefficient of restitution for balls was
5 measured using an air canon with a pressure of 45 psi. which gives a velocity of about 230 ft./sec. Values for balls can be compared from one to another, but not with the COR values for cores or the one piece balls shown below, which are measured using different conditions.
10 The test is used for general guidance to ball performance.

Examples 4 and 5 indicate that zinc oxide and a high acid ionomer give slightly superior resilience than barium sulfate and ionomer containing lower acid
15 levels. Properties of all the thermoplastic cores are acceptable, though not quite equal to that of the control thermoset core ball. Comparative Example C3 has a low Hytrel and a high ionomer level; as a result, the compression is very high. High compression values
20 indicate a high force to compress, and a ball with a 'hard' feel. Example C4 used a blend with no epoxy-containing polymer. The blend was compared with example 4 for coefficient of restitution and durability. Durability was determined by firing from an air canon at
25 the indicated pressure against a steel rebound plate, and counting the number of hits before the ball breaks. While it had a comparable coefficient of restitution, it's durability was extremely poor, indicating a strong need to compatibilize the blend with the epoxy
30 containing polymer.

TABLE 2B
MOLDING CONDITIONS FOR TWO PIECE CORES
AND ONE PIECE BALLS

5	Temperatures Degrees C.	
	Rear	183
	Center	173
	Front	173
	Nozzle	177
10		
	Mold Front/Back	10
	Melt	195
15	Pressures Kg/Square Cm	
20	Injection 1st Stage	130
	Injection 2nd Stage	110
	Injection Hold	13
Cycle Times (sec)		
25	Pack	10
	Hold	480
	Booster	10
	Cure Time	15
	Screw Retraction	5.35
30	Pad (cm)	0.6
	Screw Speed RPM	55
	Back Pressure (Kg/square cm)	
	Mold Diameter (cm)	3.88
35	*Prototype mold, limited cooling, four cavity	

EXAMPLES 7, 8, 9 AND 10 AND CONTROL EXAMPLE

These examples illustrate the use of the thermoplastic blends of the invention for use in one piece balls. The blends were made using extrusion conditions as in Table 1A. Balls were molded using conditions as in Table 2B, except that the ball diameter was 1.65 inches. Compositions are given in Table 3, and properties are shown in Table 3B.

TABLE 3
ONE PIECE BALL COMPOSITIONS

Ex#	Ref#	Hytrel	EBAGMA	Ionomer	Filler	Additive
7	136-1	H1,42(51)	G1,3(4)	I3,37(45)	F2,17	T,1
8	150-1	H2,44(52)	G1,3(4)	I3,37(44)	F2,15	T,1
9	8143-3	H1,42(52)	G1,3(4)	I2,35(44)	F4,20	-
10	H003A	H1,46(56)	G2,3(4)	I1,34(41)	F3,9.5	T,4 A1,4

Values are weight percentages. Percentages in parenthesis are on a polymer only basis.

H1,G1,G2,I1,I2,I3,F2,F3,F4,A1 as in previous tables.

H2 is a 'Hytrel' resin with composition : 27.4/7.9/44.8/19.5%:ter/isophthaloyl/PTMEG2000/1,4butane diol, plus an antioxidant.

T is TiO2, grade R960 mfg. by the DuPont Company.

TABLE 3B
PROPERTIES OF ONE PIECE BALLS

Ex#	Melt Flow (g/cc)	Dens.	%Rebound	Compr.	COR	Durability (Hits)
7	3.0	1.16	64	83	.586	>200
8	5.3	1.17	-	-	.558	-
9	13.6	1.20	67	104	.602	>200
10	-	1.12	-	88	.653	-
Control		1.14	-	100	.737	100

The control was a Wilson ULTRA two piec ball, with a thermoset butadiene core and a 'Surlyn' blend cover.

5 Coefficient of Restitution was measured using an air cannon with initial ball velocity of 180 ft./sec. The results suggest that "soft" polyetherester appears to give superior results to a harder grade (example 8), and a harder ionomer (more methacrylic acid as in example 10) is also preferred.

10

15

20

25

30

35

What is claimed is:

1. A composition comprising:
 - a) 65-90 weight percent of a thermoplastic polymer selected from copolyetheramides and copolyetheresters;
 - b) 1-10 weight percent of an epoxy-containing compound;
 - c) the remainder, to total 100 weight percent of an acid-containing ethylene copolymer ionomer.
2. The composition of claim 1 further containing about 40-60 weight percent, based on the total weight of the composition of a filler having a density greater than or equal to about 4 gm/cc.
3. The composition of claim 2 where the filler is selected from ZnO and BaSO₄.
4. The composition of claim 1, 2 or 3 where a) is a copolyetherester.
5. The composition of claim 1, 2 or 3 where b) is a glycidyl-containing copolymer.
6. The composition of claim 1, 2 or 3 where c) is an ethylene/(meth)acrylic acid copolymer.
7. The composition of claim 1, 2 or 3 where a) is a copolyetherester, b) is a glycidyl-containing copolymer, and c) is an ethylene/(meth)acrylic acid copolymer.
8. A three piece golfball comprised of a center, an elastomeric winding and a cover wherein the center comprises a composition selected from those of claim 1, 2, 3, 4, 5, 6, and 7.
9. A three-piece golfball comprising a center, an elastomeric winding and a cover wherein the center comprises about 35 weight percent (total) of a polyetherester having a shore D hardness of 40, 1-5 weight percent of an ethylene/n-butylacrylate

(28%)/glycidyl methacrylate (5%) copolymer, about 10 weight percent of an ethylene/methacrylic acid (20%) copolymer highly neutralized with Na cation, and about 50 weight percent ZnO.

5

10. A composition comprising:

10

- a) 50-65 weight percent of a thermoplastic polymer selected from copolyetheramides and copolyetheresters;
- b) 1-10 weight percent of an epoxy-containing compound; and
- c) the remainder, to total 100 weight percent, of an acid-containing ethylene copolymer ionomer;

15

provided that a) is greater than 50 volume % of the volume of the composition.

20

11. The composition of claim 10 further containing about 15-25 weight percent, based on the total weight of the composition, of a filler having a density greater than or equal to 4 gm/cc.

12. The composition of claim 11 where the filler is selected from ZnO and BaSO₄.

13. The composition of claim 10, 11 or 12 where a) is copolyetherester.

25

14. The composition of claim 10, 11 or 12 where b) is a glycidyl-containing copolymer.

15. The composition of claim 10, 11, or 12 where c) is an ethylene/(meth)acrylic acid copolymer.

30

16. The composition of claim 10, 11 and 12 where a) is a copolyetherester, b) is a glycidyl-containing copolymer, and c) is an ethylene/(meth)acrylic acid copolymer.

35

17. A two-piece golfball comprised of a core and a cover wherein the core comprises a composition selected from those of claims 10, 11, 12, 13, 14, 15 and 16.

18. A two-piece golfball comprising a core and a cover, wherein the core comprises 50-65 polymer weight percent of a thermoplastic polymer selected from polyetheramides and polyetheresters, 1-10 polymer weight percent of an epoxy-containing compound, 15-25 total weight percent ZnO and the remainder to total 100 polymer percent, of an acid-containing ethylene copolymer ionomer.

19. A two-piece golfball comprising a core and a cover wherein the core comprises 50-65 polymer weight percent of a polyetherester having a shore D hardness of about 40, 1-5 polymer weight percent of an ethylene/n-butyl acrylate (28%)/glycidyl methacrylate (5%) copolymer; 40-45 polymer weight percent of an ethylene/(meth)acrylic acid (20%) copolymer highly neutralized with Na cations, and about 20 total weight percent ZnO.

20. A composition comprising:

- 20
- a) between 30 and 50 polymer weight percent of a thermoplastic polymer selected from copolyetheramides and copolyetheresters;
- b) 1-10 polymer weight percent of an epoxy-containing compound;
- 25
- c) 15-25 total weight percent, of a filler having a density greater than about 5 gm/cc; and
- d) the remainder, to total 100%, polymer percent of an acid-containing ethylene copolymer ionomer.
- 30

21. The composition of claim 20 where a) is a copolyetherester.

22. The composition of claim 20 where b) is an ethylene glycidyl-containing copolymer.

23. The composition of claim 20 where d) is an ethylene/(meth)acrylic acid copolymer.

24. The composition of claim 20 where a) is a copolyetherester, b) is a glycidyl-containing copolymer, and c) is an ethylene/(meth)acrylic acid copolymer.

25. The composition of claim 20, 21, 22, 23 or 24 where the filler is selected from ZnO, lead silicate and tungsten carbide.

26. A two-piece golfball comprised of a core and a cover, wherein the core comprises a composition selected from those of of claim 20, 21, 22, 23, 24, and 25.

27. A composition comprising:

- a) 40 - 65 polymer weight percent of a thermoplastic polymer selected from copolyetheresters and copolyetheramides;
- b) 1-10 polymer weight percent of an epoxy-containing compound;
- c) 5-20 total weight percent of a filler having a density greater than 4 gm/cc; and
- d) the remainder, to total 100 polymer weight percent, of an acid-containing ethylene copolymer ionomer.

28. The composition of claim 27 where a) a is copolyetherester.

29. The composition of claim 27 where b) is a glycidyl-containing copolymer.

30. The composition of claim 27 where d) is an ethylene/(meth)acrylic acid copolymer.

31. The composition of claim 27 where a) is a copolyetherester, b) is a glycidyl-containing copolymer, and d) is an ethylene/(meth)acrylic acid copolymer.

32. The composition of claim 27, 28, 29, 30 or 31 where the filler is selected from ZnO and BaSO₄.

33. A one-piece golfball comprising a composition selected from those of claim 27, 28, 29, 30, 31 and 32.

34. A one-piece golfball comprising about 55 polymer weight percent of a polyester having a shore D hardness of about 40, 1-5 polymer weight percent of ethylene/n-butyl acrylate (28%/glycidyl methacrylate (5%) copolymer, 40-45 polymer weight percent of an ethylene/methacrylic acid (20%) copolymer highly neutralized with Na cations, and about 10 total weight percent ZnO.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/09168

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C08L67/02; C08L77/00; A63B37/00

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.C1. 5

C08L ; A63B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 268 287 (KANEKAFUCHI KAGAKU KOGYO KABUSHIKI KAISHA) 25 May 1988	1,4-7
A	see the whole document	2,3,8-34
A	GB,A,2 002 781 (SUMITOMO RUBBER) 28 February 1979	1
	see page 1, line 31 - line 50; claims 1-8 see page 2, line 35 - page 3, line 14	
A	GB,A,2 210 623 (MITSUBISHI KASEI CORPORATION) 14 June 1989	1
	see claims 1-8	
A	EP,A,0 382 539 (SUMITOMO CHEMICAL COMPANY LIMITED) 16 August 1990	1
	see page 5, line 4 - line 37; claims 1,2,3	
	-/-	

⁹ Special categories of cited documents: ¹⁰¹⁰ "A" document defining the general state of the art which is not
considered to be of particular relevance¹⁰ "E" earlier document but published on or after the international
filing date¹⁰ "L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)¹⁰ "O" document referring to an oral disclosure, use, exhibition or
other means¹⁰ "P" document published prior to the international filing date but
later than the priority date claimed¹⁰ "T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention¹⁰ "X" document of particular relevance; the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step¹⁰ "Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such docu-
ments, such combination being obvious to a person skilled
in the art.¹⁰ "A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

13 APRIL 1992

Date of Mailing of this International Search Report

16.04.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DECOCKER L.

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	GB,A,2 164 342 (DUNLOP LIMITED) 19 March 1986 cited in the application	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9109168
SA 55490**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 13/04/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0268287	25-05-88	JP-A- 63301250	08-12-88
		JP-A- 63130618	02-06-88
		AU-B- 614944	19-09-91
		AU-A- 8131587	26-05-88
		US-A- 4914152	03-04-90
		US-A- 4898911	06-02-90
GB-A-2002781	28-02-79	JP-C- 1113116	16-09-82
		JP-A- 54033134	10-03-79
		JP-B- 56053388	18-12-81
		US-A- 4185831	29-01-80
GB-A-2210623	14-06-89	JP-A- 1215853	29-08-89
		DE-A- 3833286	20-04-89
		JP-A- 2218738	31-08-90
EP-A-0382539	16-08-90	JP-A- 2209963	21-08-90
		CA-A- 2009626	09-08-90
GB-A-2164342	19-03-86	JP-A- 61072042	14-04-86